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CONTACT LAYER ON ENAMEL – PRECIOUS METAL INTERFACE

Yu. A. Spiridonov[1] and E. V. Tsareva[1, 2]

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The formation of a common diffusion layer in enamel – precious metal composition has not been studied adequately. The use of secondary mass spectrometry, making it possible to determine the elemental composition of adjoining layers, and electron microscopy has made it possible to determine the elemental composition of contacting layers of these materials.

Key words: enamel, corrosion, silver, bonding, coating.

The bonding force acting between an enamel coating and a metal substrate determines the longevity of enameled metal articles, including jewelry. For this reason, the study of adhesion processes between enamel melt and a substrate is important not only for industrial articles made of steel but also articles made of precious metals.

Many factors, which together comprise the adhesion process, affect the formation of a strong enamel coating on a metal substrate [1, 2].

A *mechanical bond* in metal – enamel systems is determined by bonding forces, which manifest as a result of different acting mechanisms. The penetration of enamels into a surface and the action of compression forces make possible attachment along micro-asperities and thereby bonding.

Under the action of *electrostatic coupling forces*, arising at the interface of phases as a result of the formation of contact potentials, bonding strength indicators > 10 MPa are formed and their contribution to the total bonding strength of enamel will be about 10% of the work of adhesion of oxide on metal.

Dispersion forces affect the formation of a bond between a coating and a substrate. These forces consist in interactions between particles of matter as a result of the statistical motions of charge and the formation of temporary dipoles.

The bonding of enamel with a substrate can also be explained by *chemical interaction*, which lowers the internal energy, decreases the free surface energy and makes it possible to attain chemical-thermodynamic equilibrium of the energy of bond development on the interface, if the glass is saturated with a metal oxide that is not reduced by the base-layer metal. Aside from this, it is generally assumed that the oxide layer arising on the metal surface during firing participates in the formation of a bond between the metal substrate and the enamel. This layer is coupled in a natural manner with the substrate metal, and at the same time it is chemically related to oxide glasses. For this reason, its formation greatly facilitates the adhesion of enamel to metal.

Since enameling of ferrous metals, specifically, steel, plays an especially important role in everyday life and in industry, this process has been studied quite well and described in the literature. Characteristic features of the interaction in the enamel melt – steel system are the thermodynamic instability of the iron in the melt, the ionic character of their conductivity, the nonuniformity of steel as well as the diffusion of the oxidizing agents and the removal of the products of corrosion (mainly, iron ions) into the melt. But, in the case where an enamel coating forms on the surface of jewelry alloys of gold and silver the situation can differ because of the high chemical inertness of silver and gold.

The state, structure and composition of the contacting layers of the substrate and glass during enameling of different metals largely make it possible to obtain these articles. They have been repeatedly studied by different methods, but there is practically no information in the scientific literature about these layers in the case where enamel coatings are deposited on precious metals.

Contact layers of materials were studied on compositions of enamel (containing SiO_2, PbO, K_2O, B_2O_3, BaO and ZnO) and jewelry alloys. The results of an electron microscopic study (using a JeolJSM-6510LV electron microscope), performed together with x-ray spectral phase analysis, attest to the existence of a transition contact layer between the enamel coating and the metal. In the case of an enamel – metal composition the transition layer is characterized by a nonuniform structure; the elemental composition of this layer is repre-

[1] D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia.
[2] E-mail: ellyyy@mail.ru.

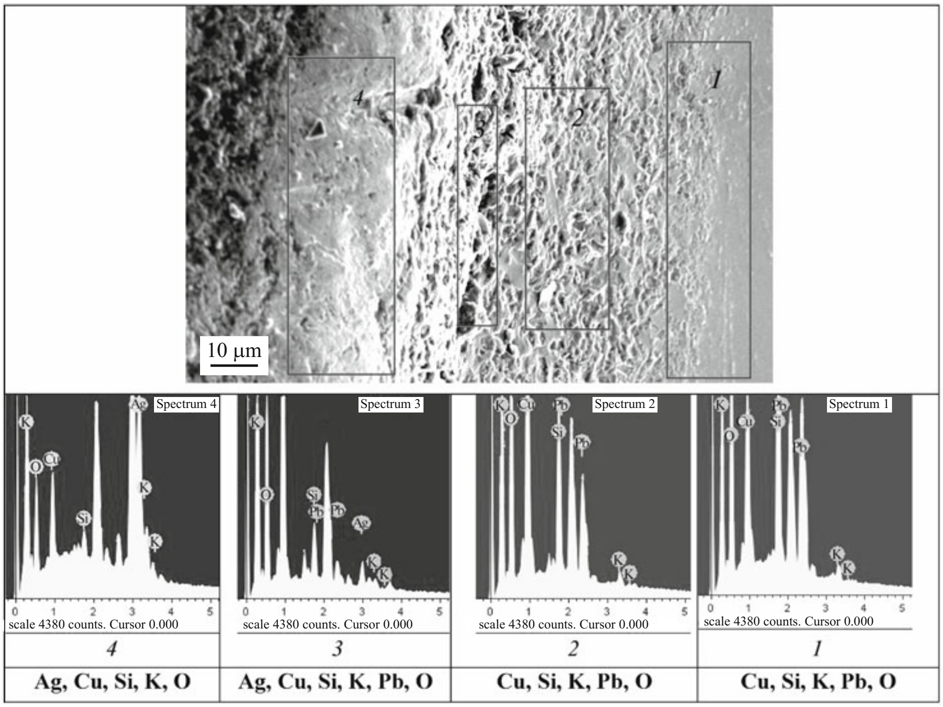

Fig. 1. Elemental composition of a sample in the enamel – silver system: *1*) enamel; *2*) boundary enamel layer; *3*) boundary layer of metal; *4*) metal.

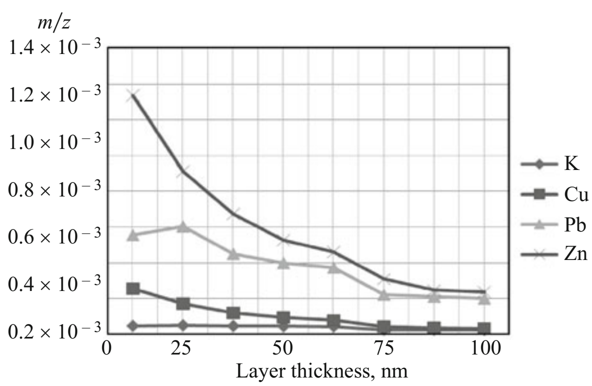

Fig. 2. Concentration distribution of the components of enamel in the contact layer.

sented as components of the jewelry alloy (Ag, Cu) and the components of enamel (Pb, Si, K) in different concentration ratios (Fig. 1). The thickness of the transition layer is 40 – 50 μm. Similar studies performed on the composition of enamel – gold showed the presence of such a 10-μm thick transition layer.

The chemical composition of the boundary layers of the contacting materials has also been studied by secondary mass-spectroscopy with material etched off in 12.2 nm thick layers. The components of enamel — lead, zinc, potassium — were found in the metal layers adjoining the contact zone. Their concentration decreases in deeper layers of the metal (Fig. 2). The components of the metal were recorded in a similar manner in the enamel layers adjoining the boundary with the metal.

In summary, studies have confirmed that a transition layer forms between the enamel coating and substrate form jewelry allows. Apparently, diffusion and physical dissolution of the components of enamel in the metal are the basis for the observed formation of a transition layer. At the same time it can be supposed that copper oxidizes to the ionic state and diffuses into the glass phase of the enamel. Apparently, the formation of a transition layer, adhesion forces and mechanical bonding of enamel on the asperities of the substrate contribute to the bonding strength.

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